



# Reprint of: RRKM reaction rate theory for transition states of any looseness<sup>☆</sup>



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## ABSTRACT

Unimolecular rate theory for various types of reactions is implemented for any looseness of transition state. Quantum states are counted for all but the “transitional” modes, their phase space being counted via Monte Carlo sampling. The rate constant  $k_{EJ}$  is then weighted with the initial  $E$  and  $J$  distributions.

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## 1. Introduction

In the transition-state theory of chemical reactions the position of the transition state along the reaction coordinate is frequently readily identifiable, for example when the potential-energy surface for the reaction has a pronounced saddle point. In this case the transition state is often chosen to be a hypersurface passing through the saddle point so as to separate the reactant and product valleys.<sup>3</sup>

In reactions such as bond fissions, the reverse reaction of free-radical recombination, or some ion–molecule reactions, there is little or no potential-energy barrier along the reaction coordinate. However, one may define a dividing surface such that the available phase space on it, restricted by any constants of the motion, is a minimum [2]. This dividing surface is then the transition state [2] and it depends on any constants of the motion, such as, for an isolated molecule or pair of molecules in the gas phase, the total energy  $E$ , the total angular momentum  $J$  and its component  $J_z$  along a space-fixed axis. In practical applications of this criterion (or in a quantum treatment) it is common to choose as a dividing surface a hyper-surface in *coordinate* space such that the number of available classical (or quantum) states  $N_{EJ}$  for motion on the hypersurface, is a minimum when plotted versus the reaction coordinate [3–5]. (This criterion was noted in Ref. [5], which mistakenly attributed it to Bunker. However, Bunker and Pattengill [6] minimized a density of states for RRKM theory rather than  $N_{EJ}$ , which is not quite correct but gives essentially the same result.)

For bond-fission reactions the main difficulty in calculating  $N_{EJ}$  lies in the “transitional” degrees of freedom, namely those vibrations, rotations, and hindered rotations in the dissociating reactant which become free rotations and orbital motions of the separating products. In the transition-state region these modes may display large-amplitude anharmonic motion and may be strongly coupled to each other. The calculation of their quantum energy levels and the associated sum of states becomes very complicated indeed. In this Letter we treat the transitional modes in a way which affords computational tractability and which makes use of coordinates designed to facilitate the analysis. Namely, action–angle coordinates related to those used for bimolecular collisions [7] are introduced for these modes. Next, a classical Monte Carlo calculation of the available phase space is made, including quantum corrections if needed. The remaining coordinates are treated via the usual quantum count [8].

The procedure, choice of variables, and some results are given below. The present work extends in a practical way that which we have given earlier [9,10] in which the transition states were assumed to be “tight” or “loose” in actual applications. Monte Carlo calculations of phase-space volumes have been used in completely classical calculations of numbers of states, densities of states, or unimolecular reaction rate theory [11–14]. Both rotating [11] and non-rotating [12–14] systems have been so studied, although for the rotating systems [11] the ensembles used were not  $J$ -fixed. A comparison between classical and quantal counts for separable [12] and non-separable [13] systems has also been given.

## 2. Theory

The rate constant  $k_{EJ}$  for the unimolecular decomposition or isomerization of a molecule with total energy in the center-of-mass frame  $E$  and specified  $J$  is given in RRKM theory [9] by

$$k_{EJ} = N_{EJ}/h\rho_{EJ}, \quad (1)$$

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<sup>3</sup> Sometimes, as in the transfer of a light particle, such as an H atom or proton between two heavy particles, the system may by-pass the saddle-point region because of the large curvature of the conventional reaction path. A treatment of such cases is given in Ref. [1].

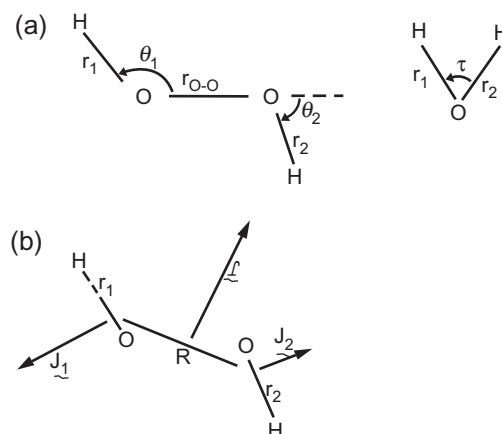
where  $N_{Ej}$  is the number of quantum states of the transition state having an energy less than or equal to  $E$  in the degrees of freedom orthogonal to the reaction coordinate and at the given  $J$ ;  $\rho_{Ej}$  is the density of states of the dissociating or isomerizing molecule. Tunneling corrections along the reaction coordinate [5,15,16] (Eq. (4) of Ref. [16]) and reaction path degeneracy [5,10,16,17] can be introduced into  $N_{Ej}$  if needed. A unimolecular rate constant at any pressure is obtained from Eq. (1) in the standard way by suitably weighting the  $E$ s and  $J$ s (Eq. (4) of Ref. [10]). In the center-of-mass system the modes are subdivided into “transitional” modes and the remaining coordinates, thereby yielding the following expression for  $N_{Ej}$ :

$$N_{Ej} = \int_0^{E'} N_v(E' - \epsilon) \Omega_j(\epsilon) d\epsilon, \quad (2)$$

where  $\Omega_j(\epsilon) d\epsilon$  is the number of states of the transitional modes for the given  $J$  when their total energy lies in  $(\epsilon, \epsilon + d\epsilon)$ .  $N_v(E' - \epsilon)$  is the number of quantum states in the remaining coordinates having an energy less than or equal to  $E' - \epsilon$ ,  $E'$  being the available energy, i.e.  $E$  minus the potential-energy minimum at the given value of the reaction coordinate and minus the zero-point energy of the modes included in  $N_v$ . The two types of coordinates are taken to be uncoupled from each other in Eq. (2), apart from an indirect coupling via the dependence of the molecular constants on the reaction coordinate.

To obtain  $N_{Ej}$  we define two sets of body-fixed coordinate axes each fixed in a separating fragment [7,18]. The origin of each coordinate system is located at the center of mass of that fragment. If either fragment has some symmetry, its coordinate axes are chosen to coincide with the symmetry axes. Using the action–angle coordinates of polyatomic species [7,18] referred to earlier to represent the phase space of the transitional modes,  $\Omega_j$  and then  $N_{Ej}$  is calculated as a function of  $R$ , the separation distance of the fragments centers of mass. Our use of action–angle rather than Cartesian coordinates is a matter of convenience rather than of necessity, chosen so as to enhance the sampling in the Monte Carlo calculation of  $\Omega_j$  and to minimize the dimensionality of the phase-space integral. These coordinates are also suitable for a scattering description of the process and, as such, are useful in describing the separated-product properties as well as exit-channel effects.

In the case of a reaction such as  $\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$  action variables, written throughout in units of  $\hbar$  as  $j_1, j_{1z}, j_{1z}, j_{2z}, l$  and  $l_z$ , and their conjugate angles can be used [7,18] to specify the relative orientations of all the atoms  $j_1$  and  $j_2$  are the individual rotational angular momentum actions of fragments 1 and 2,  $j_{1z}$  and  $j_{2z}$  are their space-fixed  $z$  components, and  $l$  and  $l_z$  are the orbital angular momentum action of the fragments and its  $z$  component, respectively. However, we choose to make a canonical transformation [18]<sup>4</sup> to the action variables  $J, J_z, j_1, j_2, l, k$  and their respective conjugate angles  $\alpha, \beta, \alpha_1, \alpha_2, \alpha_1, \alpha_k$ , where  $k$  is an intermediate angular momentum action associated with a vector sum  $|j_1 + j_2|$ , and  $J$  corresponds to  $|k + l|$ . ( $J$  now denotes an action variable rather than the angular momentum, from which it differs by a factor of  $2\pi$ .) The transformation between action–angle and internal-type coordinates, in which the potential is usually given, is similar to that described in Ref. [7] and is given elsewhere [19]. (In the case of a dissociation of a polyatomic molecule into non-linear fragments there are two additional action variables involved in the description of the transitional modes namely the component  $K_i$  of each  $j_i$  along the body-fixed  $z$  axis of fragment  $i$ . In such cases there are six transitional degrees of freedom, apart from those associated with  $J$  and  $J_z$ .)



**Fig. 1.** (a) The O–O and O–H bond lengths ( $r_{\text{O-O}}, r_1, r_2$ ); bonding angles ( $\theta_1, \theta_2$ ), and the torsional angle for  $\text{H}_2\text{O}_2$ . (b) Angular momenta for fragment rotations and relative motion of HO, OH, and distance between the centers of mass,  $R$ .

For a system described by the above variables such as  $\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$ , we have

$$\Omega_j(\epsilon) = (2J + 1) \times \int \cdots \int dj_1 dj_2 dl dk d\alpha_1 d\alpha_2 d\alpha_k \delta(\epsilon - H_{\text{cl}}), \quad (3)$$

where  $H_{\text{cl}}$  is the classical Hamiltonian for the transitional modes, and is given below. The factor  $2J + 1$  arises from the  $J_z$  multiplicity. The limits on the angle variables are 0 to 1. The angular momentum action variables are restricted by energy conservation and by the triangle inequalities:  $|j_1 - j_2| \leq k \leq j_1 + j_2$  and  $|k - l| \leq J \leq k + l$ . The relative positions of all the particles are independent of the overall orientation of the set of atoms and so the integrand cannot depend on  $J_z, \beta$  and  $\alpha$  [19].  $H_{\text{cl}}$  is taken to be

$$H_{\text{cl}} = \frac{j_1^2}{2\mu_1 r_1^2} + \frac{j_2^2}{2\mu_2 r_2^2} + \frac{l^2}{2\mu R^2} + V_t(r_{\text{O-O}}, \theta_1, \theta_2, \tau), \quad (4)$$

where  $\mu_i$  is the reduced mass of fragment  $i$ , and  $\mu$  is the reduced mass for the relative motion of the two fragments.  $H_{\text{cl}}$  is specified by the variables ( $R, r_1, r_2, j_1, j_2, l, k, \alpha_1, \alpha_2, \alpha_k$ ). The potential  $V_t$  for the transitional modes is modeled in the example below for  $\text{H}_2\text{O}_2$  to be function of the internal coordinates  $r_{\text{O-O}}, \theta_i$  and  $\tau$ , in Fig. 1a. The two other coordinates there,  $r_1$  and  $r_2$ , correspond to OH vibrations and are therefore included in  $N_v(E' - \epsilon)$ . The reaction coordinate  $R$  and several angular momenta involved in the description of  $\text{H}_2\text{O}_2$  are depicted in Fig. 1b. The functional form used for  $V_t$ , together with numerical constants, are given elsewhere [19].

From Eqs. (2) and (3) one obtains

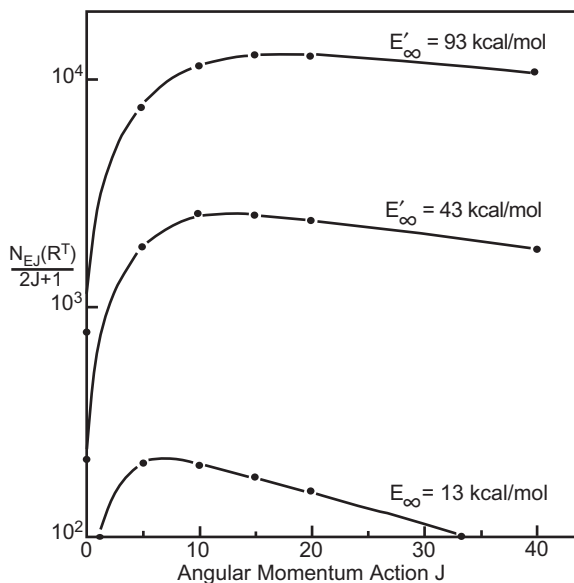
$$N_{Ej} = (2J + 1) \times \int \cdots \int N_v(E' - H_{\text{cl}}) dj_1 dj_2 dl dk d\alpha_1 d\alpha_2 d\alpha_k, \quad (5)$$

where  $N_v$  is zero unless  $E' > H_{\text{cl}}$ . The Monte Carlo evaluation of this integral involves random selection of the angles in the (0,1) interval and random selection of the angular momenta subject to the constraints described above.

### 3. Results

In developing and assessing the present method three bond-fission reactions were examined using model potential-energy surfaces:  $\text{NO}_2 \rightarrow \text{NO} + \text{O}$ ,  $\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$ , and  $\text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3$ , having 2, 4 and 6 transitional modes, respectively. For each system  $N_{Ej}$  was calculated over a range of  $E$ s and  $J$ s, and in each case the transition-state location  $R^{\text{T}}$  defining the minimum in the  $N_{Ej}$  versus  $R$

<sup>4</sup> A different but related angular momentum coupling scheme is used in Ref. [7] because of the different application involved.



**Fig. 2.** Semilog plot of  $N_{EJ}(R^T)/(2J+1)$  versus  $J$  (in units of  $h$ ) for various values of  $E'_\infty$ , the energy available to the system at  $R = \infty$ . The calculations are given for  $R = R^T$ ; the value of  $R^T$  varies with  $E$  and  $J$  and is in the range 3.0–3.75 Å.

curve was readily identifiable.  $N_{EJ}(R^T)$  was obtained to within a variance of  $\approx 1\%$  for  $\text{NO}_2$  and  $\text{H}_2\text{O}_2$  and  $\approx 3\%$  for  $\text{C}_2\text{H}_6$  with uniform Monte Carlo sampling. The relative computation times to obtain  $N_{EJ}$  for each of the three systems were found to be essentially independent of  $E$  and  $J$ . Computation times for systems larger than ethane will be approximately the same as that for ethane since the number of transitional modes is the same. Thus, large systems and large  $E$ s are readily treated.

A sample of the results is presented in Fig. 2 where  $N_{EJ}/(2J+1)$  is plotted versus  $J$  for three values of available product energy. One sees that the ordinate depends strongly on  $J$  at small  $J$  and that it undergoes a maximum with increasing  $J$  at high  $J$ s. Quantum corrections can be introduced as needed. When there are many accessible quantum states in each zeroth-order transitional degree of freedom, the quantum correction is negligible. This situation occurs when the transition state is loose or when the available  $\epsilon$  is high enough. One can estimate quantum counts using a method such as Doll's [12] or using the frequencies of the transitional modes obtained from the power spectrum [20] of a typical trajectory for  $H_{cl}$  in Eq. (4). One can also adapt quantum Monte Carlo methods [21] to a microcanonical ensemble to obtain a quantum correction for the transitional modes. From the typical value of  $\int \Omega_j(\epsilon') d\epsilon'/(2J+1)$ , integrated from 0 to  $\epsilon$ , one can roughly estimate whether quantum corrections are needed or not. When this value is of the order of unity or less, they certainly are needed. (See for example Refs. [12,13].)

In subsequent papers [19] results such as those in Fig. 2 are compared with those for simple models, e.g. the loose and tight transition states. Also explored there are the dependence of  $N_{EJ}$  and of  $R^T$  on the large- $R$  behavior of the potential-energy surface, the calculation of unimolecular and bimolecular rate constants, en-

ergy disposal cross sections, the “transition-state switching” topic in ion–molecule reactions [22], and the approximation of minimizing an appropriate ensemble-weighted average of  $k_{EJ}$ , instead of minimizing  $N_{EJ}$  for each  $E$  and  $J$ . Comparison will also be made with a statistical “adiabatic channel” model [17]. Some features of the present method for obtaining  $k_{EJ}$  are its simplicity, rapidity of computation and, particularly, its use of actual potential-energy surfaces as they become available.

## References

- [1] V.K. Babamov, R.A. Marcus, *J. Chem. Phys.* 74 (1981) 1790; V.K. Babamov, V. Lopez, R.A. Marcus, *J. Chem. Phys.* 78 (1983) 5621; V.K. Babamov, V. Lopez, R.A. Marcus, *J. Chem. Phys.* 80 (1984) 1812; B.C. Garrett, D.G. Truhlar, A.F. Wagner, T.H. Dunning, *J. Chem. Phys.* 78 (1983) 4400; D.K. Bondi, J.N.L. Connor, B.C. Garrett, D.G. Truhlar, *J. Chem. Phys.* 78 (1983) 5981.
- [2] E. Wigner, *J. Chem. Phys.* 5 (1937) 720; E. Wigner, *Trans. Faraday Soc.* 34 (1938) 29; J. Horiuti, *Bull. Chem. Soc. Japan* 13 (1938) 210; J.C. Keck, *J. Chem. Phys.* 32 (1960) 1035; J.C. Keck, *Advan. Chem. Phys.* 13 (1967) 85; D.G. Truhlar, W.L. Hase, J.T. Hynes, *J. Phys. Chem.* 87 (1983) 2664, and references therein.
- [3] W.L. Hase, *J. Chem. Phys.* 57 (1972) 730; W.L. Hase, *J. Chem. Phys.* 64 (1976) 2442; B.C. Garrett, D.G. Truhlar, *J. Chem. Phys.* 70 (1979) 1593.
- [4] M. Quack, *J. Troe, Ber. Bunsenges. Physik. Chem.* 81 (1977) 329; J. Troe, *J. Chem. Phys.* 75 (1981) 226; J. Troe, *J. Chem. Phys.* 79 (1983) 6017.
- [5] R.A. Marcus, *J. Chem. Phys.* 45 (1966) 2630.
- [6] D.L. Bunker, M. Pattengill, *J. Chem. Phys.* 48 (1968) 772.
- [7] A.F. Turfa, D.E. Fitz, R.A. Marcus, *J. Chem. Phys.* 67 (1977) 4463; A.F. Turfa, W.-K. Liu, R.A. Marcus, *J. Chem. Phys.* 67 (1977) 4468.
- [8] P.J. Robinson, K.A. Holbrook, *Unimolecular Reactions*, Wiley-Interscience, New York, 1972; W. Forst, *Theory of unimolecular reactions*, Academic Press, New York, 1973.
- [9] R.A. Marcus, *J. Chem. Phys.* 20 (1952) 359; R.A. Marcus, O.K. Rice, *J. Phys. Colloid Chem.* 55 (1951) 94.
- [10] R.A. Marcus, *J. Chem. Phys.* 43 (1965) 2658; R.A. Marcus, *J. Chem. Phys.* 52 (1970) 1018.
- [11] D.L. Bunker, *J. Chem. Phys.* 40 (1964) 1946; S.C. Parantos, J.N. Murrell, J.C. Hadjuk, *Chem. Phys.* 68 (1982) 109.
- [12] J.D. Doll, *Chem. Phys. Letters* 72 (1980) 139; L.B. Bhuiyan, W.L. Hase, *J. Chem. Phys.* 78 (1983) 5052.
- [13] D.W. Noid, M.L. Koszykowski, M. Tabor, R.A. Marcus, *J. Chem. Phys.* 72 (1980) 6169; M.V. Berry, *Ann. Phys.* 131 (1981) 163.
- [14] J.E. Adams, *J. Chem. Phys.* 78 (1983) 1275.
- [15] W.H. Miller, *J. Am. Chem. Soc.* 101 (1979) 6810.
- [16] R.A. Marcus, *J. Chem. Phys.* 45 (1966) 2138.
- [17] M. Quack, *J. Troe, Ber. Bunsenges. Physik. Chem.* 78 (1974) 240.
- [18] D.M. Wardlaw, Ph. D Thesis, University of Toronto (1982).
- [19] D.M. Wardlaw, R.A. Marcus, *J. Chem. Phys.*, to be submitted for publication.
- [20] D.W. Noid, M.L. Koszykowski, R.A. Marcus, *J. Chem. Phys.* 67 (1977) 404; M.L. Koszykowski, D.W. Noid, R.A. Marcus, *J. Phys. Chem.* 86 (1982) 2113; D.M. Wardlaw, D.W. Noid, R.A. Marcus, *J. Phys. Chem.* 88 (1984) 536.
- [21] J.A. Barker, *J. Chem. Phys.* 70 (1979) 2914; D. Chandler, P. Wolynes, *J. Chem. Phys.* 74 (1981) 4078; K.S. Schweitzer, R.M. Stratt, D. Chandler, P.G. Wolynes, *J. Chem. Phys.* 75 (1981) 1347; R.M. Stratt, *J. Chem. Phys.* 77 (1982) 2108; D. Thirumalay, E.J. Bruskin, B.J. Berne, *J. Chem. Phys.* 79 (1983) 5063; J.D. Doll, D.L. Freeman, *J. Chem. Phys.* 80 (1984) 2239; D.L. Freeman, J.D. Doll, *J. Chem. Phys.* 80 (1984) 5709.
- [22] W.J. Chesnavich, L.M. Bass, T. Su, M.T. Bowers, *J. Chem. Phys.* 74 (1981) 2228; M.T. Bowers, M.F. Jerrold, W. Wagner-Redeker, P.R. Kemper, L.M. Bass, *Faraday Discussions Chem. Soc.* 75 (1983) 57.